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CERAMIC GREEN MIXES BASED ON MODIFIED CLAYEY SUSPENSIONS

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It is established that the modifier content — chemically modified bottoms from the distillation of kaprolaktam (MBDK) — plays a considerable role in the liquation of ceramic green mixes. Liquation occurs for 0.5 – 1.0% MBDK, while above 1.0% the clay surface becomes hydrophobic as a result of its interaction with organic matter.

Key words: clayey suspension, modifiers, ceramic green mixes, rheological properties.

Electrolytes, surfactants, water-soluble salts, as well as various plasticizers influence the properties of clayey suspensions and the structural and rheological properties of ceramic green mixes.

Organic matter and plasticizing additives are widely used in various areas of ceramic technology to stabilize and improve the properties of water solutions, impart to the required molding properties of the plastic molding mixes based on clay-containing initial materials and nonplastic materials, as well as giving the required strength to the molded blanks in wet and dry states. At the same time superplasticizers are being more widely used and new modifiers based on reliable raw materials resources and wastes from the chemical industry are being developed [1 – 3].

We propose a new modifier for clays and clayey suspensions which is based on wastes from the production of kaprolaktam — chemically modified bottoms from the distillation of kaprolaktam (MBDK), whose composition and chemical structure were determined in previous investigations.

The modifier obtained is a salt with a polymeric cation and anion of mineral acids. The general formula of the modifier has the following form:

$$-[\mathrm{H}_2^+\mathrm{N}-(\mathrm{CH}_2)_6-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-]_n X^-,$$

where $n = 1 – 5$, and X^- is the anion of the acid (Cl^-, NO_3^-, HSO_4^-) [4].

On the basis of the aggregate state this is a stable uniform thick paste that is capable of remaining uncrystallized for a long time, and is soluble in water.

Highly concentrated dispersed systems with three-dimensional structure exhibit the most complex rheological properties. The formation and change of these structures which occur as a result of physical – chemical, colloidal – chemical, biochemical, or physical processes always change the rheological properties of the structures.

We investigated the effect of MBDK on the rheological properties of clayey suspensions based on clays with kaolin-montmorillonite and kaolin-hydromicaceous mineral compositions and kaolin KAKh-2 (GOST 19607–74), which are ground to specific density 1400 m^2/kg. The investigations were performed with a Reotest-2 rotational viscosimeter with coaxial cylinders.

The rheological flow curves of kaolin-montmorillonite and kaolin-hydromicaceous clays are presented in Fig. 1. Evidently, the initial suspensions are viscoplastic bodies with quite high maximum shear stress and strain-rate dependent effective viscosity, characteristic for strongly structured systems. The flow of such bodies is described most completely by Ostwald's equation

$$\tau = k\dot{\gamma}^n,$$

where τ is the shear stress, Pa; is the deformation rate, sec^{-1}; and, k and n are coefficients.

The character of the rheological flow changes with increasing MBDK content. For average content of the MBDK additive (0.5 – 0.8%[3]) the linear part of the curves increases

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[3] Here and below — the content by weight.

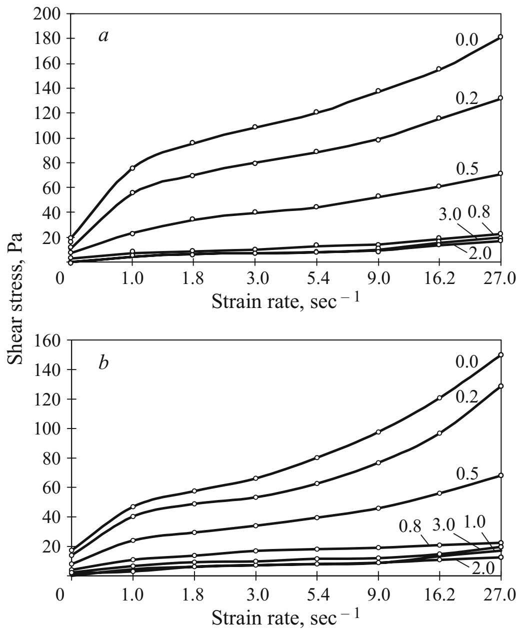

Fig. 1. Shear stress versus the strain rate for kaolin – montmorillonite (*a*) and kaolin – hydromicaceous (*b*) clays. The numbers on the curves correspond to the modifier content by weight (wt.%).

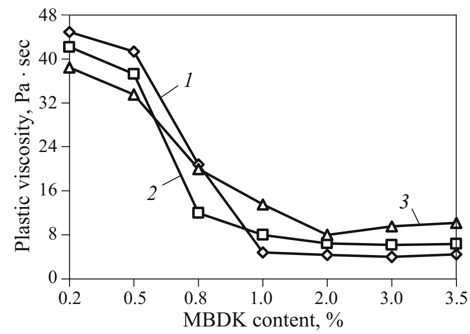

Fig. 2. Plastic viscosity versus MBDK content: *1*, *2*) kaolin-montmorillonite and kaolin-hydromicaceous clays, respectively; *3*) kaolin.

and the flow is described by the Bingham – Shvedov equation:

$$\tau = \tau_0 + \eta_{pl}\dot{\gamma},$$

where τ_0 is the limiting shear stress, Pa, and η_{pl} is the plastic viscosity, Pa · sec.

As the content of the MBDK additive increases to 0.8% the effect of the strain rate on the change of the shear stress weakens and remains practically unchanged with 1.0 – 3.0% modifier. The plastic viscosity of the clayey suspensions (Fig. 2) at first decreases sharply with the MBDK content increasing from 0.2 to 1.0%, reaching a definite minimum value, and then with 1.0 – 3.0% modifier added it remains unchanged and even increases for a kaolin suspension, while the fluidity of the suspensions of the kaolin-montmorillonite and kaolin-hydromicaceous clays decreases.

Visually, stratification of the suspension with separation of the dispersion medium (water) as a result of the destruction of the structure is observed. After the modified clay is filtered and dried at 105°C, hydrophobic properties manifest and such clay is highly hydrophobic; the wetting angle is in the range $0.61 < \cos\theta < 0.57$.

Comparing the rheological flow curves of the kaolin-montmorillonite and kaolin-hydromicaceous compositions and kaolin shows that depending on the type of clay the region of the liquefying effect shrinks when MBDK is introduced. The greatest liquefying effect occurs for kaolin montmorillonite clay and the smallest effect occurs for kaolin. The MBDK content greatly affects the liquefaction process for suspensions. Thus the suspensions liquefy for 0.5 – 1.0% modifier content, while above 1.0% the surface of the clay particles becomes hydrophobic. Such clay is best used in the production of water-free molding mixes, as active fillers of polymers and resins, for lubrication-cooling liquids, preparation of petroleum-based boring solutions, and other applications.

The physic-mechanical properties of MBDK-based plastic clay mixes of kaolin-montmorillonite clay were studied for 29 mm in diameter and 26 mm high samples. Clay with a definite dispersity was dried at 105°C to a constant mass and mixed with water to a paste with plastic consistency. The modifier was introduced into the mixing water in amounts 0.2 – 3.0%. The compositions of the clay mixes are presented in Table 1.

The samples were molded by plastic pressing, dried in 48 h to moisture content 10 – 12%, and fired at 950°C in a SNOL-1.6 furnace. The physic-mechanical properties of the samples are presented in Table 2.

Analysis of the data in Table 2 shows that introducing 0.2 – 1.0% MBDK increases the density and strength of the samples, while for modifier content above 1.0% the strength and density of the samples decrease. This can be explained by the fact that firing increases the porosity of the samples because the organic part of the modifier is burned out.

TABLE 1.

Composition	Content of additive in the clay,* wt.%	
	MBDK	water
1	No additive	21.0
2	0.2	17.4
3	0.5	15.9
4	0.8	14.4
5	1.0	13.2
6	2.0	12.2
7	3.0	10.0

* Above 100%.

TABLE 2.

Composition	MBDK addition, %	Sample density kg/m^3	Sample strength, MPa
1	0	1763	13.4
2	0.2	1770	16.7
3	0.5	1823	17.8
4	0.8	1854	18.1
5	1.0	1897	18.3
6	2.0	1891	18.0
7	3.0	1887	17.5

The proposed mechanism of the interaction of MBDK with a clay surface can be represented as follows. The MBDK molecules are displaced by adhesion forces into the interpacket space of the layered silicates, which clays are, especially montmorillonite clays. Becoming fixed on the surface of clay particles they impede adsorption of water molecules and they also replace water in the interlayer space, which weakens the contact interaction between the clay particles, and peptization of the particles occurs at the same time. When 0.5 – 1.0% modifier is added, the suspension liquefies, the viscosity decreases, and the fluidity increases. When the MBDK content increases above 1.0%, the water molecules are completely displaced from the interpacket space, and the volume polymeric modifier cation, interacting with a negative clay particle, imparts special properties to it. As result of these processes the clay loses its intrinsic hydrophyllic properties and, conversely, acquires affinity to nonpolar liquids, which makes it possible to obtain stable suspensions on its basis.

In summary, substantial liquefaction of ceramic pastes occurs with 1.0% content of MBDK. The composition obtained on their basis can be recommended for manufacturing ceramic brick.

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